

Structure and Electronic Excitations in Organometallic Transition Metal Complexes

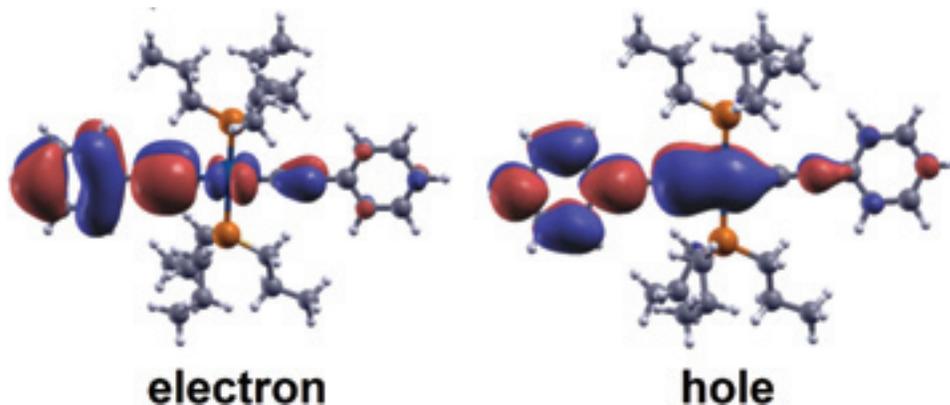
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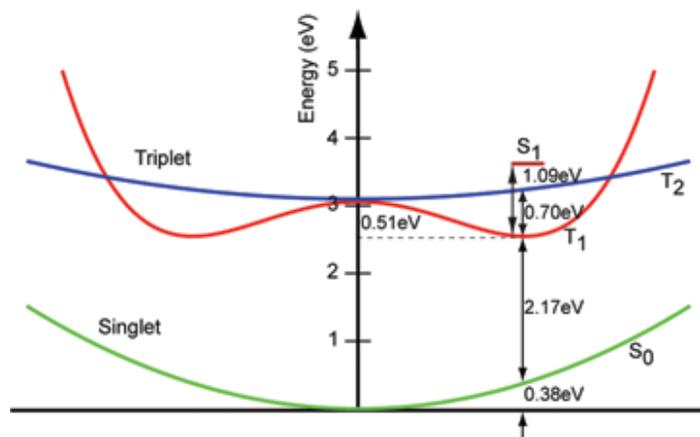
In support of energy programs at the Laboratory, we have been studying the photophysics of Pt-acetylide complexes of interest in the context of the next-generation-lighting initiative, as well as the behavior of molecular systems that mimic Nature's ability to split water into its elemental components. A hydrogen-based economy is feasible only if hydrogen is produced from nonfossil sources. Therefore, molecular systems capable of splitting H_2O using solar energy only have been the focus of our research. To find new, more efficient luminescent materials, we have been studying with researchers within and external to the Laboratory new molecular systems currently being used for organic light-emitting diodes (OLEDs) and for new types of nanowires. The set of materials based on platinum-acetylide π -conjugated oligomers has prompted great interest in recent years for their potential applications in highly efficient organic electroluminescent devices [1]. In these compounds the π -orbitals of the ligands are conjugated with the d orbitals of the Pt allowing for charge migration along the oligomers. Electroluminescence

in these materials might also be expected to be reasonably efficient, as the presence of the metal and the consequent spin-orbit coupling would allow both singlet and triplet electron-hole pairs to recombine emissively, an option not available to purely organic polymers due to the strong enforcement of spin selection rules in the light atoms.

In a collaboration with experimentalists in Los Alamos' Bioscience Division and the University of New Mexico we have studied the behavior of electronic excitations in platinum-acetylide complexes. The hybrid density functional theory (DFT) results were analyzed via the computational technique of Natural Transition Orbitals (NTOs) developed at the Laboratory [2]. As shown in Fig. 1, phosphorescence in the platinum monomer comes from a triplet state localized on one side of the molecule, which generally goes by the name of the 2nd order Jahn-Teller effect. This localization stems from a coupling between the electronic state and the vibrational modes of the molecule. After absorption of energy there are two nearly degenerate excited states that can mix with each other upon a geometric deformation of b_{3u} symmetry. Figure 2 shows the energy landscape of the excited states of the molecule which couples the two electronic states. Using linear response theory (commonly referred in the literature as time dependent DFT, TD-DFT) we were able to estimate the barrier for charge migration of the electronic excitation and the phosphorescence emission energy. The latter is in good agreement with experiment [3]. The former led us to predict that the charge

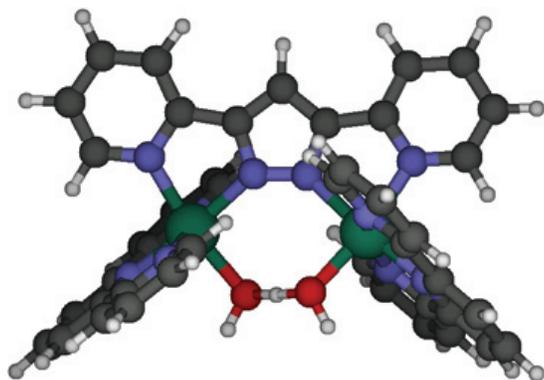
Fig. 1. The electron and hole pair in the lowest excited state spontaneously localizes on one half of the molecule. This is due to a coupling of the electronic state with a phonon mode that causes the molecule to deform along a b_{3u} mode breaking the symmetry of the molecule. The ethynyl triple bond is weakened in the excited state because of one of the electrons being promoted from the π bonding orbital to a π^* anti-bonding orbital which leads to a signature in the experimental infrared spectrum.



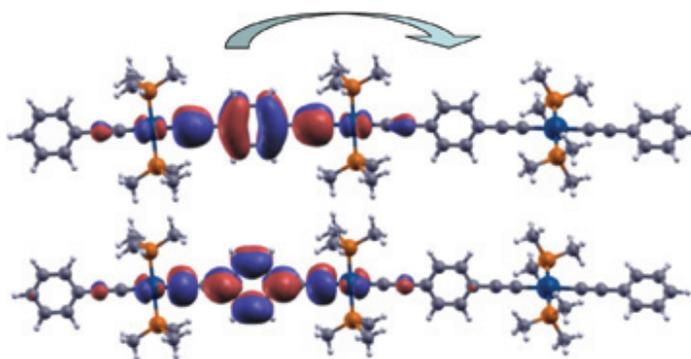


migration in these systems will be via an activated hopping mechanism with a barrier of 0.5 eV. This localization persists in longer oligomers. Figure 3 shows the lowest electronic excitation for the platinum-trimer, which also spontaneously localizes on a phenyl ring.

Water oxidation catalysts such as the blue dimer $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ (1) and the recently discovered $[Ru_2^{II}(bpp)(trpy)_2(H_2O)_2]^{3+}$ (2) continue to stir interest in the context of water converting into its constituents for the production of molecular hydrogen using only solar energy. We have studied both these molecules using *ab-initio* techniques. For complex 1 our calculations of vibrational frequencies aided experimental groups in Los Alamos' Materials Science and Technology Division and the University of North Carolina in the interpretation of UV-vis and Raman spectra. In complex 2



ruthenium dimer (see Fig. 4). This explains the lowering in pK_a observed by Sens et al. [4].



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Fig. 2. Energy landscape for the electronic excitation of $Pt(P^{t}Bu)_3)_2(ethylnylbenzene)_2$ calculated via linear response theory (TD-DFT). The calculated energies are in good agreement with the measurements of Liu and coworkers [5].

Fig. 3. In longer oligomers the electron and hole pair in the lowest excited state also localizes spontaneously on one phenyl ring and neighboring ethynyl groups. The conjugation of the excited-state orbital with the d orbital on the platinum facilitates the migration of the excitation. This migration happens via an activated hopping with activation barrier of about 0.60 eV.

Fig. 4. Optimal structure of the hydroxo-aqua state of $[Ru_2^{II}(bpp)(trpy)_2(OH_2)(OH)]^{3+}$. Upon deprotonation of complex 2, we observed that a hydrogen bond network is formed in the solvent next to the ruthenium dimer. This explains the lowering in pK_a observed by Sens et al. [4].